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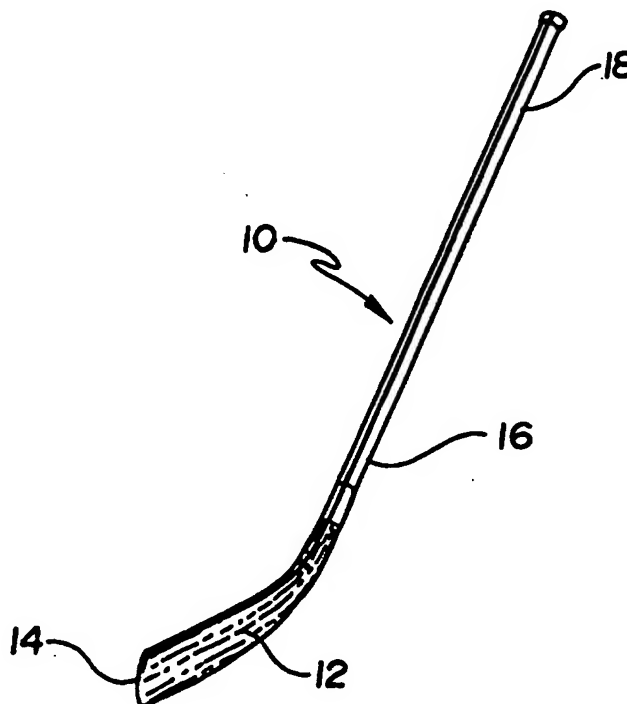
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With international search report.

(54) Title: NON-SKID WATER BASED COATING

(57) Abstract

The use of water-based polyurethane as a non-skid coating for gripping surfaces and tread surfaces on tools and sporting equipment, such as a hockey stick (10) having a water-based polyurethane coating (12) covering the blade portion (14), the stick portion (16), and the grip portion (18).



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NON-SKID WATER BASED COATING

Background of the Invention

This invention relates to a new use for water dispersed polyurethanes which are well known. For example, water dispersed polyurethanes are described in a co-pending application, serial number 08/101,430, filed August 3, 1993 entitled "An Anionic Water Dispersed Polyurethane Polymer For Improved Coatings and Adhesives", which application was filed in the name of the inventor of the subject invention. The subject matter of that co-pending application is incorporated herein in its entirety by reference.

Summary of the Invention

This invention is concerned specifically with the recognition that coatings of aqueous polyurethane dispersions when combined with gripping areas or tread areas on sporting equipment, tools, and the like, particularly when the polyurethane exhibits elastomeric characteristics, will provide an improved non-skid contact surface.

Brief Description of the Figures

Figure 1 shows a hockey stick coated according to the invention.
Figure 2 shows a baseball bat coated according to the invention.
Figure 3 shows a surfboard coated according to the invention.
Figure 4 shows a hockey glove coated according to the invention.

Detailed Description of the Invention

Any polyurethane dispersible in aqueous medium may be used as a non-skid coating in accordance with this invention. Generally, in a preferred form, a dispersible polyurethane exhibiting elastomeric characteristics is preferred.

Aqueous dispersed polyurethanes are generally prepared by reacting a polyester or polyether based polyol, a diisocyanate, and water loving groups (hydrophiles) which render the resulting polymer dispersible in water. In accordance with the prior art, such a polymer is typically prepared as a pre-polymer which is then chain extended in water with a soluble amine.

As already indicated, for the purpose of this invention, a most preferred form of the water dispersed polyurethane is one which exhibits elastomeric characteristics *i.e.* an aqueous polyurethane elastomer. Aqueous polyurethane elastomers are high molecular weight oligomers which have been modified with water loving groups (hydrophiles) rendering them water dispersible. This technique produces high performance polymers reducing the use of volatile organic compounds to provide environmentally friendly compounds having unique "stroft" (strong but soft) characteristics lending them particularly useful as non-slip grip aides and tread aids on sporting equipment, tools, and the like. An example is a polyether based polyurethane dispersion which will be described specifically in more detail below.

Generally, however, elastomeric characteristics are preferred for the purposes of this invention as already stated. From HACKH'S CHEMICAL DICTIONARY, "An elastomer is a generic term for all substances having the properties of natural, reclaimed, vulcanized, or synthetic rubber, *q.v.*, in that they stretch under tension, have high tensile strength, retract rapidly, and recover their original dimensions fully. Typical elastomers contain long polymer chains". The preferred polyurethane dispersion elastomers *i.e.*, water dispersible polyurethanes described for this invention are soft elastomers with excellent tensile and tear strength. These properties are best created using new polyols, from OLIN CORPORATION of Stanford, Connecticut 06904 known as POLY-L™ POLYOLS. OLIN CORPORATION has developed this new line of POLY-L™ polyols containing very low levels of terminal unsaturation. In polyol synthesis, the formation of terminally unsaturated end groups results in a substantial loss in hydroxy functionality. Chains containing terminal unsaturation are monofunctional, containing only one hydroxyl group per chain. These monofunctional chains act as stoppers in polymer formation and decrease the resultant properties of the polyurethanes. By the use of an organometallic catalyst, such as a double metal cyanide, POLY-L™ polyols may be prepared with high levels of polyol and very little monofunctionality. OLIN'S POLY-L™ polyol series is the preferred polyol for improving non-skid characteristics with aqueous polyurethane elastomers in accordance with this invention.

In conventional polyols, which are prepared with KOH catalysis, the amount of unsaturation formed increases as a direct function of the equivalent

weight. In contrast, with the organometallic catalysts used to prepare the POLY-L™ polyols, the amount of unsaturation formed increases very slowly with the equivalent weight (Figure 1). The use of organometallic catalysts allows the synthesis of ultra high molecular weight polyols with low unsaturation levels and functionality very close to the theoretical values. No residual metals are detected in the polyols at a detection limit of <1 ppm.

TABLE 1

Typical properties of POLY-L™ triols:			
POLY-L™ POLYOL	(1)	(2)	(3)
Hydroxyl No. (mg KOH/g)	29	18	17
Unsaturation	0.017	0.02	0.02
Water (% by weight)	0.03	0.03	0.03
Acid No. (mg KOH/g), max.	0.05	0.05	0.05
ph in 10/6 IPA/water	6	6	6
Viscosity @ 25°C, cps	1800	3000	3000
Specific gravity			
@ 25°C/25°C	1.0234	1.0101	1.0132
Flash point, * COC			
(°C)	230	221	223
(°F)	446	430	433
Density @ 25°C (lb./gal)	8.52	8.41	8.44
% Primary OH	80	-	55
Residual Metals (ppm)	0	0	0

EXAMPLE

This example is an aqueous polyurethane dispersion which provides a very flexible yet strong film. The flexibility of this polymer was measured using a tensiometer and determined to be around 2,200%. This defines its ability to stretch or grow in length. The polymers tensile strength, resistance of a material to a force tending to tear it apart, was 3,100 pounds per square inch. Technical data regarding physical properties are provided in Table 2 herein below.

TABLE 2

TYPICAL PHYSICAL PROPERTIES AND GENERAL INFORMATION	
RAW MATERIAL BASE	Polyurethane
5 COLOR, WET	Hazy
COLOR, DRY	Clear
SOLIDS	35%
PH	7.8
WEIGHT PER GALLON	8.7 pounds
10 TENSILE	3100 psi
ELONGATION	2200%

The "stroft" properties make aqueous polyurethane elastomers particularly useful as grip enhancing coatings for sporting equipment and the like. For example, an application which showed very good results was coating handles on baseball bats. To help improve the grip on wooden baseball bats, players often tape or apply tacky-oily substances like pine tar. In this invention, an aqueous polyurethane elastomer may be spray applied on a wooden bat handle and dried. The clear, colorless dried film renders outstanding non-slip characteristics for grip. Also, besides improving the grip, such coatings "stroft" (strong but soft) properties make it a very durable coating unlike pine tar and tape.

Likewise, such coatings may be used with advantageous results on hockey sticks. Hockey sticks are used in cold conditions making a fiberglass coated blade or a plastic blade very hard and brittle. A puck is difficult to control with such blades and they are likely to shatter on impact. The relatively softer, non-tacky coatings of the present invention are advantageous in this connection making the puck not only easier to handle with the coating applied to the blade but also adding tremendously to its strength and improved flexibility.

When the coating is applied to the stick proper including the gripping area, tape is no longer needed. Players usually apply tape to soften the grip and add strength to the handle of the stick. Unfortunately, tape often wears or falls off the

stick making it hazardous to the players. The coatings of the invention exhibit very good adhesion along with water resistance, and cold weather properties.

In view of the above, in connection with hockey sticks, it can be seen that the coating of the invention may be used to advantage not only to improve gripping surfaces of the hockey stick but to include its strength as well, particularly at the blade portion thereof.

The preparation of this exemplary and most preferred elastomeric polyurethane dispersion will now be described. To a reaction flask is charged 361.75 gm (.181 Eq) POLY-L 220-28 which is a polyether based polyol from OLIN CORPORATION, 120 Long Ridge Rd., Stamford, Ct 06904, 31.75 gm (.474 Eq) dimethylolpropionic acid, 33 gm n-methylpyrrolidone (optional), .27 gm DABCO T-12 which is a tin catalyst supplied by Pacific Anchor, and 120.2 gm (1.08 Eq) isophorone diisocyanate. This mixture is heated between 90-95 dec C until %NCO=3.2. This prepolymer is cooled to 80 deg C and charge with 22.74 gm (.224 miles) triethylamine. After stirring 5 minutes, the prepolymer is added to 904.4 gm (50.24 moles) de-ionized water and dispersed with gentle agitation. To this is charged a premix blend containing 10.9 gm (.36 Eq) ethylenediamine chain extender in 15 gm (.83 mole) de-ionized water. The resulting polymer properties can be seen in Table 2 above.

The invention has applicability to the following exemplary areas of sporting equipment as listed in the Table 3 herein below.

TABLE 3

	Tennis Rackets	Canoe Paddles
	Golf Clubs	Coat the palms of baseball gloves
25	Surf Boards	Coat the palms of hockey gloves
	Skate Boards	Ski Poles
	Pool Sticks	Ping Pong Paddles
	Hockey Sticks	Snow Boards
	Baseball Gloves	Mountain climbing rope
30	Screw Driver Handles	Boards that carpenters walk on and the like
	Hammer Handles	Ladders
	Saw Handles	

Referring now to the Figures, Figure 1 shows a hockey stick generally designated at 10 having a coating 12 covering a blade portion 14, the stick portion 16 and the grip portion 18. In accordance with the invention, the coating may be
5 advantageously applied to any one of these portions of the stick, to any two of them, or to all three thus in effect, coating the entire stick. Figure 2 shows a baseball bat generally designated 20 having a coating 22 on the gripping area thereof. Figure 3 shows a surfboard designated 30 having a non-skid tread area 32 on a portion thereof in the form of coating according to this invention. Figure 4 is a hockey
10 glove generally designated 40 having a palm surface area 42 coated according to this invention.

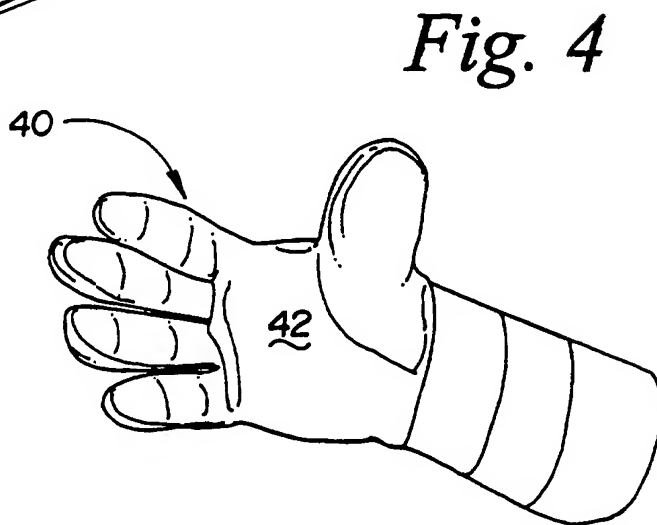
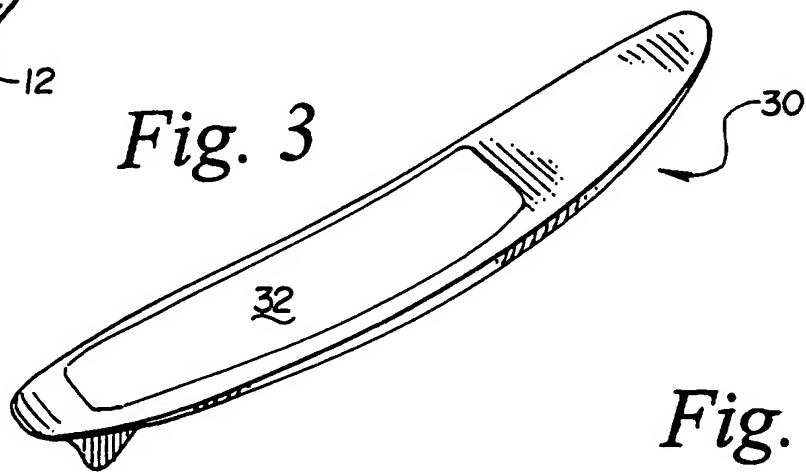
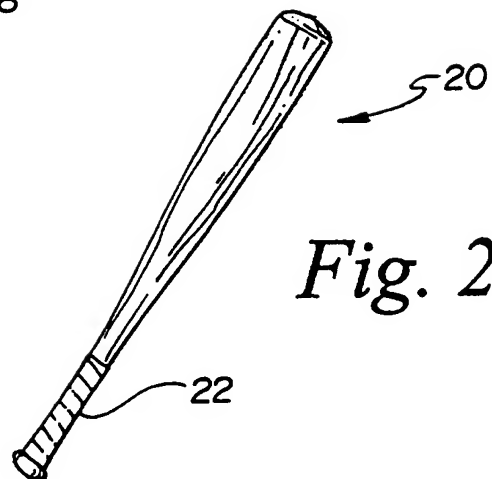
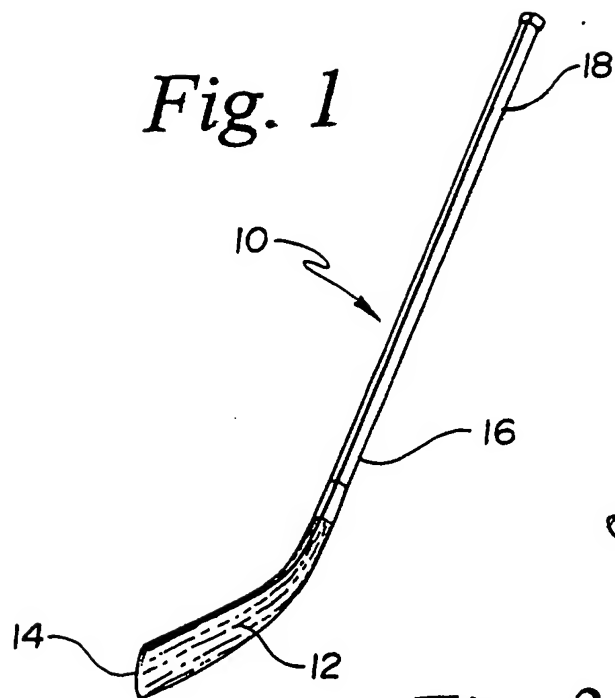
Many other articles will be readily apparent which can be provided with a coating according to this invention for improving the non-skid characteristics, gripping characteristics and so forth in connection with gripping and tread function.
15

The above Examples and disclosure are intended to be illustrative and not exhaustive. These examples and description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are intended to be included within the scope of the attached claims. Those familiar
20 with the art may recognize other equivalents to the specific embodiments described herein which equivalents are also intended to be encompassed by the claims attached hereto.

What is claimed is as follows:

1. As a non-skid coating on sports equipment, tools, equipment, and the like, particularly gripping surfaces thereof, a water based polyurethane.
2. The article of claim 1 wherein the water based polyurethane is comprised of
5 polyol and diisocyanate.
3. The article of claim 2 wherein the polyol is selected from the group consisting of polyester and polyether based polyols.
4. The article of claim 1 wherein the polyurethane has elastomeric characteristics.
- 10 5. The article of claim 1 as a hockey stick having the coating on the blade.
6. The article of claim 5 wherein the coating is on the handle.
7. An article according to claim 1 having the coating on a tread surface.
8. An article according to claim 1 wherein the polyurethane is elastomeric, and comprised of the following composition: polyether based polyol, propionic acid and
15 a diisocyanate treated with triethylamine and then combined to form a prepolymer chain extended in water with ethylenediamine.
9. As a non-skid coating for articles, a water based polyurethane coating.
10. As a non-skid tread coating for articles, a water based polyurethane coating.

1/1



INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US95/00125
A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : 428/423.2, 423.1, 425.1, 425.8, 908.8; 273/75, 81R, 57.2, 67A, 67DB; 524/591; 528/61

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/423.2, 423.1, 425.1, 425.8, 908.8; 273/75, 81R, 57.2, 67A, 67DB; 524/591; 528/61

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, search terms: (polyurethane# or urethane#), (handle# or grip? or bat# or stick# or club# or racket#), (nonskid- or non-skid: or nonslip- or non-slip).

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,269,516 (JANES) 14 December 1993, see entire document.	1, 6, 9
A	US, A, 4,284,275 (FLETCHER) 18 April 1981, see entire document.	1, 6, 9
Y	US, A, 4,801,644 (COOGAN) 31 January 1989, Abstract; column 1, lines 23-35; column 5, lines 5-27.	1-10
Y, P	US, A, 5,332,212 (SUSI ET AL) 26 July 1994, Abstract; column 3, lines 5-11.	1, 4, 5, 9
Y	US, A, 4,196,243 (SACHS ET AL) 01 April 1980, column 1, lines 23-35; column 2, lines 34-37.	7, 10

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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Date of the actual completion of the international search 06 MARCH 1995	Date of mailing of the international search report 06 APR 1995
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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,828,898 (BAILEY) 09 May 1989, column 1, lines 43-48.	7, 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/00125

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

B32B 27/00, 27/40; C08J 7/00; C08L 75/00; C08G 18/10, 18/32; A63B 49/08, 53/14, 67/04, 59/00

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